

Lecture 31. The Variation Principle

The variation theorem says that the expectation value of the energy for *any* wave function is equal to or greater than the ground state energy. This result provides a very powerful means of obtaining an upper bound on the true ground state energy. The proof is simple. Let $|i\rangle$ be a complete set of (unknown) energy eigenfunctions with eigenvalues E_i ($i = 0, 1, 2, \dots$). Let $|\psi\rangle$ be some trial wave function that you are free to guess. So long as $|\psi\rangle$ has the correct boundary conditions, we can expand it in the energy basis:

$$|\psi\rangle = \sum_{i=0} c_i |i\rangle$$

Assuming that $|\psi\rangle$ is normalized, the expectation value of the energy is

$$\langle E \rangle = \sum_i \sum_j c_i^* c_j \langle i | H | j \rangle = \sum_i \sum_j c_i^* c_j E_j \langle i | j \rangle = \sum_{i=0} |c_i|^2 E_i$$

Since $E_i \geq E_0$,

$$\langle E \rangle \geq \sum_{i=0} |c_i|^2 E_0 = E_0$$

This result gives us a method for calculating an upper bound to the ground state energy: Simply guess $|\psi\rangle$ and calculate its energy. In the event that $|\psi\rangle$ is not normalized, we can do so on the spot:

$$\frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} \geq E_0$$

Illustration: Solve for the ground state energy of the H atom with $l = 0$.

In atomic units, $H = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{1}{r}$

Let's try the wave function $\psi = e^{-r^2}$

Taking the appropriate derivatives, we find

$$H\psi = -2r^2 e^{-r^2} + 3e^{-r^2} - \frac{1}{r} e^{-r^2}$$

Evaluating the energy of this state,

$$\langle E \rangle = \frac{\int (-2r^4 e^{-2r^2} + 3r^2 e^{-2r^2} - r e^{-2r^2}) dr}{\frac{1}{8} \sqrt{\frac{\pi}{2}}} = \frac{3}{2} - 2\sqrt{\frac{2}{\pi}} = -0.096$$

The actual value of $E_0 = -1/2$.

Can we do better? Pick a better trial function. For example $\psi = e^{-\lambda r^2}$. Repeating the calculation with λ as a constant, we get

$$\langle E \rangle = \frac{3}{2} \lambda - \sqrt{\frac{2}{\pi}} \sqrt{\lambda}$$

Solving for the lowest possible value of the energy gives

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial \lambda} &= \frac{3}{2} - 2\sqrt{\frac{2}{\pi}} \sqrt{\lambda} \\ \lambda &= \frac{8}{9\pi} \\ E_{\min} &= -\frac{4}{3\pi} = -0.424 \end{aligned}$$

This is an example of the use of Gaussian functions to calculate energies and wave functions.

Another example is the He atom. To make sure that the Pauli Exclusion Principle is satisfied, we must use Slater determinants. For the two-electron case, the spin and spatial parts factor, and we needn't worry about the spin when applying the Variation Principle. The simplest possible trial wave function is the product of two hydrogenic functions. For the ground state of He we will use 1s functions,

$$\psi_{1s}(r) = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

To allow for screening, we will replace $Z=2$ with a free parameter, λ , and the trial function for the entire atom (in atomic units) is

$$\psi = \frac{\lambda^3}{\pi} e^{-\lambda(r_1+r_2)}$$

The Hamiltonian in atomic units is

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} = H_0(r_1) + H_0(r_2) + \frac{1}{r_{12}}$$

We have to calculate the matrix elements for each of the three terms of H . The first two are simply the ordinary hydrogen atom Hamiltonian for the individual electrons, but with a nuclear charge of 2, giving

$$\langle 1s(r_1)|H_0|1s(r_1)\rangle = \langle 1s(r_2)|H_0|1s(r_2)\rangle = \frac{\lambda^2}{2} - 2\lambda$$

The third term is the repulsion energy of the two electrons. It can be evaluated analytically as a series of products of spherical harmonics. The result is

$$\langle \psi(r_1, r_2)|1/r_{12}|\psi(r_1, r_2)\rangle = \frac{5\lambda}{8}$$

Putting the pieces together,

$$\langle E \rangle = \lambda^2 - \frac{27}{8}\lambda$$

$$\frac{d\langle E \rangle}{d\lambda} = 2\lambda - \frac{27}{8}$$

$$\lambda = \frac{27}{16}$$

We see that there is significant screening. The minimum energy is -2.848 au, as compared with the true value of -2.9037 .

One can do still better by assuming a more highly parameterized trial function. The cost in doing this is that the calculus becomes very messy. Is there an easier way? Choose a *superposition* of well-behaved functions, and let the variational parameters be coefficients of the superposition. In this case, all the equations are linear.

$$\psi = \sum_{i=1}^n c_i |i\rangle$$

We define the overlap integral

$$S_{ij} = \langle i|j\rangle$$

This integral need not necessarily be δ_{ij} , depending on the choice of functions. We similarly define the matrix elements

$$H_{ij} = \langle i|H|j\rangle$$

As before, we evaluate the expectation value of the energy, $W \equiv \langle E \rangle$, expressed in terms of c_i , S_{ij} , and H_{ij} :

$$W = \frac{\sum_i \sum_j c_i c_j H_{ij}}{\sum_i \sum_j c_i c_j S_{ij}}$$

We next solve for the minimum of W with respect to all the c_i . The result is a determinantal secular equation:

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & H_{13} - S_{13}W & \cdot \\ H_{21} - S_{21}W & H_{22} - S_{22}W & H_{23} - S_{23}W & \cdot \\ H_{31} - S_{31}W & H_{32} - S_{32}W & H_{33} - S_{33}W & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0$$

Solve for n roots, which give the upper bounds to the n lowest eigenvalues of H . Once we have the roots, we can go back to the algebraic equations and solve for the coefficients.

For example, in the 2x2 problem, we have

$$\begin{aligned} (H_{11} - S_{11}W)c_1 + (H_{21} - S_{12}W)c_2 &= 0 \\ \frac{c_2}{c_1} &= -\frac{H_{11} - S_{11}W}{H_{21} - S_{12}W} \\ c_1^2 + c_2^2 &= 1 \end{aligned}$$

Application: The Stark effect in the H atom. The Hamiltonian, in atomic units, is

$$H = H_0 - Fr \cos\theta,$$

where H_0 is the Hamiltonian of the field-free Hamiltonian, and F is the strength of the electric field. We will choose normalized eigenfunctions of H_0 as our variational functions, so that $S_{ij} = \delta_{ij}$. To be specific, we will take $n=2$, with

$$\begin{aligned} |1\rangle &= |1s\rangle \\ |2\rangle &= |2p_z\rangle \end{aligned}$$

By straightforward integration, we get

$$\begin{vmatrix} H_{11} - W & H_{12} \\ H_{12}^* & H_{22} - W \end{vmatrix} = \begin{vmatrix} -\frac{1}{2} - W & -2^{15/2} F / 3^5 \\ -2^{15/2} F / 3AZ^5 & -\frac{1}{8} - W \end{vmatrix} = 0$$

The result is a quadratic equation in W , with the solution

$$W_{\pm} = -\frac{5}{16} \pm \frac{3}{16} \sqrt{1 + \frac{2^{23}}{3^{12}} F^2}$$

Recall that F is expressed in atomic units, so typically, $F \ll 1$. In that limit, the ground and excited state energies are

$$W_- = -\frac{1}{2} - \frac{2^{18}}{3^{11}} F^2 = E_{1s} - 1.4798 F^2$$

$$W_+ = -\frac{1}{8} + \frac{2^{18}}{3^{11}} F^2 = E_{2p} + 1.4798 F^2$$

Lecture 32. Application to Molecules

The simplest molecule is the H_2^+ ion. If we make the Born-Oppenheimer approximation, the Schrodinger equation may be solved analytically in spheroidal coordinates,

$$\lambda = \frac{r_A + r_B}{R}$$

$$\mu = \frac{r_A - r_B}{R}$$

In this coordinate system, the wave function is separable,

$$\psi = L(\lambda)M(\mu)e^{im\phi}$$

Note that the wave function is cylindrically symmetric and is an eigenfunction of \hat{L}_z .

The simplest useful trial function allows the electron to reside on either nucleus. We will assume for this purpose a linear combination of atomic orbitals (LCAO), and for now will use only two orbitals:

$$\psi = c_A \psi_{1s}(r_A) + c_B \psi_{1s}(r_B) = c_A |A\rangle + c_B |B\rangle$$

We choose the individual orbitals to be orthonormal. This allows us to set $S_{AB} = \delta_{AB}$, and the secular equation is

$$\begin{vmatrix} H_{AA} - W & H_{AB} - WS_{AB} \\ H_{AB} - WS_{AB} & H_{AA} - W \end{vmatrix} = 0$$

This equation reduces to

$$H_{AA} - W = \pm (H_{AB} - ES_{AB})$$

$$W_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}}$$

Within the Born-Oppenheimer approximation, the Hamiltonian is

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

The first two terms are the ordinary Hydrogen Hamiltonian centered at nucleus A, which we denote as H_0 with eigenvalue $-1/2$. The last term is the internuclear repulsion, which is a constant at each fixed value of R . We ignore it in the variational calculation and just add it at the end.

We can obtain by inspection the contributions to the matrix elements from H_0 :

$$\begin{aligned}\langle A|H_0|A\rangle &= -\frac{1}{2} \\ \langle A|H_0|B\rangle &= -\frac{1}{2}S_{AB}\end{aligned}$$

The rest of the calculation is done using spheroidal coordinates. (This is not difficult). The result is

$$\begin{aligned}S_{AB} &= e^{-R}\left(1 + R + \frac{R^2}{3}\right) \\ H_{AA} &= -\frac{1}{2} - \frac{1}{R}\left[1 - e^{-2R}(1 + R)\right] \\ H_{AB} &= -\frac{S_{AB}}{2} - e^{-R}(1 + R)\end{aligned}$$

Let's look at the limiting behavior, ignoring the nuclear repulsion term:

$$R \rightarrow \infty$$

$$\begin{aligned}S_{AB} &\rightarrow 0 \\ H_{AA} &\rightarrow -\frac{1}{2} \\ H_{AB} &\rightarrow 0 \\ W &\rightarrow -\frac{1}{2}\end{aligned}$$

This is the result for a hydrogen atom.

$$R \rightarrow 0$$

$$\begin{aligned}
S_{AB} &\rightarrow 1 \\
H_{AA} &\rightarrow -\frac{1}{2} \\
H_{AB} &\rightarrow -\frac{3}{2} \\
W_- &\rightarrow -2
\end{aligned}$$

This is the result for a helium ion.

The results at intermediate distances are shown in the figures taken from Slater. We see that the ground state is bound, with a minimum near 2 au. The various figures show:

1. Electronic energy levels as a function of R. At large R the levels become localized.
2. Electronic wave functions as a function of R. These are molecular orbitals.
3. Potential energy curves with and without nuclear repulsion.

We can substitute the solutions for W back into the secular equation and obtain the LCAO coefficients. We find readily that $c_A = \pm c_B$, and the normalization integral gives $\sqrt{2(1 \pm S_{AB})}$. This leads to the two lowest molecular orbitals,

$$\begin{aligned}
\psi_{1\sigma_g}(r_A, r_B; R) &= \frac{1}{\sqrt{2(1 + S_{AB})}} \{ \psi_{1s}(r_A) + \psi_{1s}(r_B) \} \\
\psi_{1\sigma_u}(r_A, r_B; R) &= \frac{1}{\sqrt{2(1 - S_{AB})}} \{ \psi_{1s}(r_A) - \psi_{1s}(r_B) \}
\end{aligned}$$

We can demonstrate the normalization as follows:

$$\int |\psi_{1s}(r_A) \pm \psi_{1s}(r_B)|^2 d\tau = \int |\psi_{1s}(r_A)|^2 d\tau + \int |\psi_{1s}(r_B)|^2 d\tau + 2 \int |\psi_{1s}(r_A)\psi_{1s}(r_B)| d\tau = 2 + S_{AB}$$

The wave functions have two types of symmetry:

1. Axial symmetry, with quantum number $m = 0, 1, 2, \dots$ corresponding to $\sigma, \pi, \delta, \dots$ states.
2. Inversion symmetry, corresponding to g and u states.

Lecture 33. Perturbation Theory

A completely different approach is to partition the Hamiltonian into a zero-order part, \hat{H}_0 , which has known eigenfunctions and eigenvalues, and a small perturbation, \hat{H}' . We introduce a perturbation parameter, λ , such that

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'.$$

The eigenfunctions and eigenvalues are

$$\begin{aligned}\hat{H}_0\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(0)} \equiv E_n^{(0)}|n\rangle \\ \hat{H}\psi_n &= E_n\psi_n\end{aligned}$$

We next expand ψ_n and E_n in Taylor series in λ :

$$\begin{aligned}\psi_n(x, \lambda) &= (\psi_n)_{\lambda=0} + \left(\frac{\partial\psi_n}{\partial\lambda}\right)_{\lambda=0} \lambda + \frac{1}{2}\left(\frac{\partial^2\psi_n}{\partial\lambda^2}\right)_{\lambda=0} \lambda^2 = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots \\ E_n(\lambda) &= (E_n)_{\lambda=0} + \left(\frac{\partial E_n}{\partial\lambda}\right)_{\lambda=0} \lambda + \frac{1}{2}\left(\frac{\partial^2 E_n}{\partial\lambda^2}\right)_{\lambda=0} \lambda^2 = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\end{aligned}$$

We substitute both of these equations into the Schrodinger equation, and equate terms of equal powers of λ . The result is a series of correction terms for ψ_n and E_n in the limit of $\lambda \rightarrow 1$. In the special case that E_n is not degenerate,

$$\begin{aligned}E_n^{(1)} &= \langle n|\hat{H}'|n\rangle \equiv H'_{nn} \\ E_n^{(2)} &= \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} \\ \psi_n^{(1)} &= \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}\end{aligned}$$

The degenerate case involves a secular equation.

Example: The anharmonic oscillator:

$$\begin{aligned}\hat{H}_0 &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \\ \hat{H}' &= cx^3 + dx^4\end{aligned}$$

We must be careful here because \hat{H}' contains both a first order and a second order term. The first order perturbation corrections give $\langle n|x^3|n\rangle = 0$ and $\langle n|x^4|n\rangle \neq 0$. To stop here, however, as does Levine, is erroneous because the second order perturbation term for x^3 is comparable in magnitude to the first order correction for x^4 . Levine gets the wrong sign for the anharmonicity by ignoring the x^3 part of the potential.

Another example is the He atom. For the ground state,

$$\begin{aligned}\hat{H}_0(r_1, r_2) &= \hat{H}_0(r_1) + \hat{H}_0(r_2) \\ \hat{H}'(r_1, r_2) &= \frac{1}{r_{12}} \\ \psi_1^{(0)}(r_1, r_2) &= \left(\frac{Z^3}{\pi}\right) e^{-Z(r_1+r_2)} \\ E_1^{(0)} &= -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \\ E_1^{(1)} &= -Z^2 + \frac{5Z}{8} = 2.75au\end{aligned}$$

The variation method does a better job than first order perturbation theory.

The Stark effect is a bit trickier. The first order Stark correction for the 1s state is zero. To evaluate the first order Stark effect for $n = 2$ requires dealing with a 4-fold degeneracy. The answer is first order in F . The second order Stark effect for 1s corresponds to an *induced* dipole.

$$E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

The first term in this series is produced by the $2p_z$ state, with a value

$$E_1^{(2)} \approx \frac{|\langle 1s | F \cos \theta | 2p_z \rangle|^2}{E_{1s}^{(0)} - E_{2p_z}^{(0)}} = -\frac{\left(\frac{2^{15}}{3^{10}}\right) F^2}{3/8} = -\frac{2^{18}}{3^{11}} F^2$$

This is identical to the result of variation method without adjustable parameters.